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Claims

1. A mat powder coating, wherein polyester (A) polycondensated by using, as main constituents (components), a diol-constituent containing 5 - 100 wt% of at least 1-component diol selected from 2-butyl-2-ethyl-1,3-propanediol or 2,2-diethyl-1,3-propanediol, and a carboxylic-acid constituent of at least 1-component selected from terephthalic acid or isophthalic acid, and substantially non-gelled polyester (B) composed of isophthalic acid and trimethylolpropane or a constituent mainly consisting of them, and a hardening agent (C), have been mixed, and wherein the mixing rate of the constituent (A) and the constituent (B) is 30 : 70 ~ 85 : 15 in case of weight ratio.
2. A mat powder coating, wherein the molecular weight of the polyester (A) described in Claim 1 is 500 ~ 20000 and the hardening agent (C) is block-isocyanate.

Detailed description of the invention:

(Industrial field of application)

The present invention relates to a mat powder coating which gives a mat coating-film(s) by a polyester-based resin and which is excellent in adhesion to metals, water-resistance, heat-resistance and impact-resistance.

(Prior arts)

In case of Japan, powder coatings began to be used in 1970 ~ 1971. In that age, they were put in practical use for electrical appliances, kitchen utensils, extinguishers, fences, marine containers, etc., and gradually, they came to be used also for electrical home-appliances, exterior coatings of motorcars, etc.

Powder coatings can be divided into thermosetting-resin powder coatings and thermoplastic-resin powder coatings, depending on characteristics of synthetic resin(s) used as a material(s). The resins used for thermosetting-resin powder coating are an epoxy resin, acrylic resin, polyester resin, polyurethane resin, etc. The resins used for thermoplastic-resin powder coatings are a vinyl-chloride resin, polyamide, polyester, etc. which have been being used.

Powder coatings are now being used in many fields including electrical home-appliances, motorcars and construction-materials. However, as regards coated surfaces, in some cases, luster is required from a viewpoint of beauty, and in other cases, matness (flatness) or semi-matness is required.

As methods of preparing such mat powder-coatings, known are a method of adding a large amount of pigment coarse in grains, a method (Patent Publication No. 1986-19668) of dry-blending 2 kinds of powder coatings, viz. a polyester powder coating and an acrylic-powder coating, and a powder coating(s) (Patent Laid-

Open No. 1988-154771 and Patent Publication No. 1983-8429)
prepared by mixing polyester using neopentylglycol.

(Problems to be solved by the invention)

However, in the event that a large amount of pigment coarse in grains is added, there is such a problem that the smoothness and mechanical strength of coating-film(s) are lowered. With reference to the method of dry-blending 2 kinds of powder coatings, any mat coating cannot be obtained in the 1-stage of the preparation, and the coating-producing cost is high. Moreover, there also exists such a problem as changes in the blending-rate. In case of the polyester using neopentylglycol, a coating can be obtained in the 1-stage, and such a problem as the blending rate is solved, but water-resistance, heat-resistance, adhesion to metals and impact-resistance are insufficient.

(Means for solving problems)

The inventors laid eyes on such matters and studied eagerly, and as a result, they found that a mat powder coating(s) which is excellent in smoothness, water-resistance, heat-resistance, adhesion to metals and impact-resistance can be obtained by mixing a special polyester resin. And, the present invention has been completed.

Namely, the present invention relates to a mat powder coating, wherein polyester (A) polycondensated by using, as main constituents (components), a diol-constituent containing 5 - 100 wt% of at least 1-component diol selected from 2-butyl-2-ethyl-1,3-propanediol or 2,2-diethyl-1,3-propanediol, and a carboxylic-acid constituent of at least 1-component selected

from terephthalic acid or isophthalic acid, and substantially non-gelled polyester (B) composed of isophthalic acid and trimethylolpropane or a constituent mainly consisting of them, and a hardening agent (C), have been mixed, and wherein the mixing rate of the constituent (A) and the constituent (B) is 30 : 70 ~ 85 : 15 in terms of weight ratio.

The glycol constituent constituting the polyester (A) is at least 1-component diol selected from 2-butyl-2-ethyl-1,3-propanediol or 2,2-diethyl-1,3-propanediol. Though not especially limited, in addition to this diol, it is possible to contain a small amount of other glycols, e.g. aliphatic glycols such as ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, neopentylglycol, 1,4-butanediol, 1,5-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, etc., and trivalent or more polyols such as glycerol, pentaerythritol, etc. Furthermore, the carboxylic-acid constituent mainly consists of at least 1-component carboxylic-acid selected from terephthalic acid or isophthalic acid. For copolymerization, it is possible to use a required amount of other aromatic dicarboxylic-acid such as 2,6-naphthalene-dicarboxylic-acid, aliphatic dicarboxylic-acid such as adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonamethylene-dicarboxylic acid, decamethylene-dicarboxylic-acid, undecamethylene-dicarboxylic-acid, dodecamethylene-dicarboxylic-acid, tridecamethylene-dicarboxylic-acid, tetradecamethylene-dicarboxylic-acid, and alicyclic dicarboxylic-acid such as 1,4-cyclohexane-dicarboxylic-acid, etc., and trivalent or more aromatic carboxylic-acid such as trimellitic acid, pyromellitic acid, etc. as the case may be.

The carboxylic-acid constituent of the polyester (B) mainly consists of isophthalic acid. For copolymerization, it is possible to use, at need, a required amount of other carboxylic acids, e.g. aromatic dicarboxylic-acid such as terephthalic acid, 2,6-naphthalene-dicarboxylic-acid, etc., aliphatic dicarboxylic-acid such as adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonamethylene-dicarboxylic acid, decamethylene-dicarboxylic acid, undecamethylene-dicarboxylic-acid, dodecamethylene-dicarboxylic-acid, tridecamethylene-dicarboxylic-acid, tetradecamethylene-dicarboxylic acid, etc., and alicyclic dicarboxylic-acid such as 1,4-cyclohexane-dicarboxylic-acid, etc., and trivalent or more aromatic carboxylic-acid such as trimellitic acid, pyromellitic acid, etc. as the case may be. Besides, the glycol constituent mainly consists of trimethylolpropane. However, it is possible to contain, at need, a small amount of other polyvalent alcohols, e.g. aliphatic glycols such as ethyleneglycol, diethyleneglycol, 1,2-propanediol, 1,3-propanediol, neopentylglycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,3-pentanediol, etc., and trivalent or more polyol such as glycerol, pentaerythritol, etc.

It is necessary that the polyester (B) is a substantially non-gelled polyester. The "substantially non-gelled polyester" mentioned herein means a polyester which can be pulverized (smashed) by a pulverizing machine and which has fluidity when melted. If it has been gelled, it is difficult to make it into a coating (paint), and further, uniform surfaces cannot be brought about when made into a coating-film(s).

In the present invention, it is desirable that the molecular weight of the polyester (A) is in the range of 500 ~ 20000. If less than 500, the mechanical strength of the coating film is low, and further, the effect for matness is insufficient. There is such a tendency. If more than 20000, the surface of a coating film becomes uneven, and the smoothness is low. There is such a tendency. Furthermore, it is preferable that the polyester (A) and the polyester (B) have the softening point of 50 ~ 150 °C. If the softening point is lower than 50°C, the pulverized resin is condensed and is easy to solidify, and the anti-blocking property is poor. There is such a tendency. On the other hand, if higher than 150°C, the mixing and kneading temperature is made high, and the reaction with the hardening agent is propelled. As a result, the smoothness and mechanical strength are lowered. There is such a tendency.

In the case of the polyester for mat powder coatings, the mixing rate is 30 : 70 ~ 85 : 15 in terms of weight ratio, and preferably 40 : 60 ~ 80 : 20. If not in this range, the effect for materials is insufficient.

Using the above carboxylic acid and/or the alkylester thereof and glycol as materials, it is possible to prepare the polyester (A) and the polyester (B) by performing, at need, polycondensation after conducting publicly-known esterification-reaction or ester-exchange reaction. As the ester-forming derivatives of the above carboxylic-acids, enumerated are, for example, the lower alkylester of dicarboxylic acid, phenylester, acid-anhydride, halogenide, etc. However, especially, lower alkylester is preferable. As the typical concrete examples, enumerated are terephthalic acid, adipic-acid dimethyl, etc.

As the hardening agent (C), usable are an isocyanate compound, melamine compound, acid anhydride, etc. However, in view of the appearance of coating-film(s), low-temperature hardening property, etc., an isocyanate compound, especially block-isocyanate, is preferable. As the preferable block-isocyanate, enumerated are isophoronediiisocyanates blocked by ϵ -caprolactam, e.g. the B-1065, B-1530, etc. made by Hüls (phonetic). It is necessary that the amount of the hardening agent (C) to be used is an amount of functional groups just about corresponding to the amount of hydroxyl groups and is preferably in the range of 1.0 : 0.8 ~ 1.0 : 1.2.

In regard to the mat powder coating of the present invention, additive(s) for coatings can be added at need. As such additives, enumerated are, for example, pigments, run-adjusting agents, stabilizers, etc. As the above pigments, enumerated are, for example, white pigments such as zinc white, lithopone, zirconium oxide, titanium oxide, etc.; black pigments such as baryta, chalk, clay, talc, silica white, alumina white, gypsum, bentonite, etc.; gray pigments such as zinc powder, lead suboxide, etc.; red pigments such as iron oxide red, minium, vermilion, molybdate orange, antimony vermilion, toluidine red, etc.; brown pigments such as amber, iron oxide, etc.; yellow pigments such as Hansa Yellow, benzidine yellow, chrome yellow, synthetic ochre, etc.; green pigments such as copper-phthalocyan green, chromium green, chromium oxide green, zinc green, etc.; blue pigments such as copper-phthalocyanine blue, Berlin blue (iron blue), ultramarine blue, cobalt blue, manganese blue, etc.; purple pigments such as oxazine violet, manganese purple, cobalt purple, mars purple, etc.; metallic-powder pigments such as aluminium powder, copper powder,

gold powder, brass powder, etc. As the run-adjusting agents, enumerated are, for example, silicone resin, acrylic resin, fine-powder of silicon oxide, polyvinyl-butylal, organic bentonite, stearic-acid-zinc aluminium, stearic-acid zinc, etc. As the stabilizers, enumerated are, for example, oxidation-inhibitors, ultraviolet-ray absorbers, etc. The mixing rate of such additives for coatings can be optionally selected depending on kinds, but ordinarily, it can be a mixing rate used hitherto. For example, the pigment(s) is 0.5 ~ 50 wt% against the total materials, preferably 1 ~ 40 wt%, and the run-adjusting agent is 0.5 ~ 50 wt% against the total materials, preferably 5 ~ 30 wt%. The total amount thereof should not exceed 50 wt%. The stabilizer to be added should be 5 wt% or less against the total materials, preferably 1 wt% or less.

The present-invention method of manufacturing a mat powder coating is shown below. The obtained polyester (A) and the polyester (B) and the hardening agent (C) and additives (agents to be mixed) for coatings are kneaded using a kneader or rolls at 70 ~ 150°C after being uniformly mixed, and this mixture is pulverized by an ordinary mechanical method. In the case of the mechanical method, in the first stage, coarse pulverization is ordinarily done by a pulverizer, and in the second stage, fine powder is made by a fine-powder making machine. The coarse pulverization can also be done at a low temperature lower than 0 °C. For example, fine powder can easily be obtained by being pulverized while being cooled by liquid-nitrogen.

The powder coating thus obtained is stable at ordinary temperature, and blocking-phenomenon is not caused.

The powder coating of the present invention is applied to a metal-surface pre-treated in advance, by a powder coating

method, e.g. any of electrostatic spraying, fluidized soaking, electrostatic soaking, spreading (scattering), etc., and is baked at a temperature of 150 ~ 300°C, preferably 180 ~ 240 °C. By the baking, the resin is melted to form a uniform coating-film.

(Example)

The present invention is concretely described below based on examples and comparative examples. The characteristic values in the examples were measured by the following method.

The average molecular-weight was obtained from an ester value(s) by alkali hydrolysis.

The hydroxyl group value was obtained by measuring by a potassium hydroxide solution after performing the acetylation.

The softening point was obtained through visual observation while heating by a hot-plier.

On a 1-mm thick metal-plate, a coating-film of 50-60 μm was formed, and the following evaluation was done.

Smoothness: The smoothness of the coating-film was found through visual observation.

The 60° specular gloss (luster) was found (measured) pursuant to the JIS K 5400.

The pencil hardness was found in conformity with the JIS K 5400.

Cross-cut adhesion test: The coating film was cut with a cutter-knife up to such a depth as to reach the metal surface, in order to form checkers of 1mm-intervals (lengthwise and sideways). Out of 100 squares, the number of the coating films adhering to the metal surface without being peeled was expressed (counted).

Erichsen test: On a 1mm thick metal-plate, a coating film was formed. The metal plate was pushed from the reverse side by a punch of 20 mm in the diameter, and the pushing distance at the point of time when the coating film was cracked and peeled was expressed (measured).

Water-resistance: The results were marked by the following:

- : When a coating-film test-piece was soaked for one week in flowing water (room temperature), the coating-film did not change at all compared to that before being soaked.
- △ : Partially changed
- X : Remarkably changed

Heat-resistance: The results were marked by the following:

- : When a coating-film test-piece was kept vertical and stationary for one hour at 200°C, it did not change at all compared to that before being heated.
- △ : Partially changed
- x : Remarkably changed

Impact-resistance: A coating-film test-piece was put horizontally. Thereonto, a 500g striker with a 1/2 inch spherical tip was dropped from a certain height, and the height at the time when remarkable change was not caused was measured.

Synthesis examples

Preparation of polyester (A)

The compounds shown in Table 1 were put into a

stainless-steel reactor and were heated up to 250 °C, and the produced water was continuously removed, and put outside the reactor system. Subsequently, 5.84 parts by weight of antimony trioxide was added as a catalyst, and the polycondensation reaction was done for 4 hours at 280°C with the pressure-reducing degree kept at 0.5 mmHg or less, to obtain the highly polymerized polyester resins 2 and 3.

Preparation of polyester (B)

The compounds shown in Table 1 and 4.39 parts by weight of zinc acetate as a catalyst were put into a stainless reactor and were heated up to 230 °C, and the produced water was continuously removed, and put outside the reactor system. Subsequently, the pressure-reducing degree was kept at 600 mmHg or less for 3 hours, to obtain the highly polymerized polyester resin 4.

Preparation of polyester (D)

The compounds shown in Table 1 were treated as done in the case of the polyester (A), to obtain the polyester resin 1.

The physical properties of the respective polyester resins were also shown in Table 1 together.

Examples 1 ~ 2, comparative examples 1 ~ 2

The polyester resins, hardening agent, leveling agent, benzoin and titanium oxide shown in Table 2 were taken at the rate shown in Table 3 and were dry-blended by a Henschel (phonetic) mixer. Then, the mixture was melted and kneaded at 100 °C, cooled and pulverized, and was separated by a 145-mesh sieve, to obtain a powder coating of 145 mesh or less.

The obtained powder-coating was applied on a zinc-phosphate coated steel-plate and was baked for 20 minutes at 200°C so that the thickness of the coating film might be 50 ~ 60 μ m.

The performance of each coating-film was evaluated, and the obtained results are shown in Table 3.

It can be obviously seen from Table 3 that the products in the Examples 1 and 2 have the effect for matness (flatness) and that the coating films have excellent physical-properties compared to those in the comparative examples.

(Effect of the invention)

With reference to the special powder-coating of the present invention, in addition to excellent matness, coating-films with various physical-properties which could not be obtained in the case of prior mat powder-coatings, viz. adhesion to metals, water-resistance, heat-resistance, impact-resistance, etc., can be obtained; and it can be used in many fields including electrical home-appliances, motorcars and construction-materials.

Table 1

Polyester resin No.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Composition (parts by weight)				
Terephthalic acid	16600	16600	16600	
Isophthalic acid				16600
Ethyleneglycol	3720			
Neopentylglycol	10400			
2,2,-diethyl-1,3-propanediol			13200	
2-butyl-2-ethyl-1,3-propanediol		25600		
Trimethylolpropane				16520
Physical properties	Average			
	molecular weight			
	3730	3400	3400	1280
	Hydroxyl group			
value (mgKOH/g)	30	29	30	285
	Softening			
point	78	57	66	76

Table 2

	<u>Examples</u>		<u>Comparative examples</u>	
	<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>
Composition (parts by weight)				
Polyester (D) 1			45	28
Polyester (A) 2	45			
Polyester (A) 3		45		
Polyester (B) 4	20	20	20	28
Block-isocyanate (C) (1)	35	35	35	44
Leveling agent (2)	1	1	1	1
Titanium oxide	50	50	50	50
Benzoin	0.5	0.5	0.5	0.5

(1) Brand name B-1530 made by Hüls (phonetic)

(2) Brand name Acronal 4F (phonetic) made by BASF

Table 3

<u>Physical properties of coating-films</u>	<u>Examples</u>		<u>Comparative examples</u>	
	<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>
Smoothness	Good	Good	Good	Good
60°C specular gloss (%)	7	7	7	7
Impact-resistance (cm)	70	60	50	40
Pencil hardness	2H	2H	2H	3H
Heat-resistance	○	○	△	△
Cross-cut adhesion test	100/100	100/100	80/100	75/100
Water-resistance	○	○	△	△
Erichsen (mm)	8	6	3	3